

If you no longer need this publication write to the Geological Survey in Washington for an official mailing label to use in returning it

**UNITED STATES DEPARTMENT OF THE INTERIOR**

**THE ACTION OF SOME AQUEOUS  
SOLUTIONS ON CLAYS OF THE  
MONTMORILLONITE GROUP**

**GEOLOGICAL SURVEY PROFESSIONAL PAPER 197-F**



UNITED STATES DEPARTMENT OF THE INTERIOR  
Harold L. Ickes, Secretary  
GEOLOGICAL SURVEY  
W. C. Mendenhall, Director

---

Professional Paper 197—F

---

THE ACTION OF SOME AQUEOUS  
SOLUTIONS ON CLAYS OF THE  
MONTMORILLONITE GROUP

BY  
P. G. NUTTING

---

Shorter contributions to general geology, 1941-42  
(Pages 219-235)



UNITED STATES  
GOVERNMENT PRINTING OFFICE  
WASHINGTON : 1943

---

For sale by the Superintendent of Documents, Washington, D. C. . . . . Price 10 cents

## CONTENTS

	Page		Page
Abstract.....	219	Solubility of montmorillonite clays in alkaline solutions..	230
Introduction.....	219	Electrodialysis of hydrosols.....	230
Solubility of silica.....	220	Summary and conclusions.....	232
Solubility of montmorillonite clays in acid solutions.....	222	Index.....	235
Discussion of data.....	223		
Interpretation of data.....	229		

## ILLUSTRATIONS

	Page		Page
FIGURE 23. Solubility of opaline silica in water at different temperatures.....	221	FIGURE 28. Polkville bentonite in hydrochloric acid solutions.....	226
24. Solubility of silica in hydrochloric acid solutions.....	221	29. Quincy clay (Florida fuller's earth) in hydrochloric acid solutions.....	228
25. Wyoming bentonite in hydrochloric acid solutions.....	225	30. Soil in hydrochloric acid solutions.....	228
26. Wyoming bentonite in oxalic acid solutions.....	225	31. Filtrol (activated bentonite) in hydrochloric acid solutions.....	229
27. Japanese acid clay in hydrochloric acid solutions.....	226	32. Wyoming bentonite in sodium carbonate solutions.....	231

# THE ACTION OF SOME AQUEOUS SOLUTIONS ON CLAYS OF THE MONTMORILLONITE GROUP

By P. G. NUTTING

## ABSTRACT

This experimental investigation of the solubility of several types of montmorillonite clay covers the range of acid and alkali concentration from 0 to 4 percent, using two liters of solvent and excess clay. Each solubility-concentration curve changes slope in its central portion (0.2 to 0.6 percent), the variation being characteristic of the type of montmorillonite. Silica dissolved exceeds the saturation limit (about 0.4 gram per liter) over a range of concentration probably due to partial recombination as silicate micellae. Dissolved sesquioxides are partly water insoluble silicates and partly soluble salts. The results are discussed and their interpretation suggested.

## INTRODUCTION

Silicates of the montmorillonite-beidellite group are much more easily attacked by dilute acids than those of the kaolin, mica, talc, or pyrophyllite groups. They have been chosen for study for this reason and because they are the more active constituents of many soils and are readily available in nearly pure form in the bentonites. The study of their chemical behavior promises to throw light on the different processes of weathering and the formation of plant food in soils as well as on mineral replacement and alteration.

The bases of the montmorillonite clays are removable by digestion in hot 20 percent (6 normal) hydrochloric acid for a few hours, leaving behind isotropic silica. In pure water these clays dissolve to the extent of at least 36 parts per million even after repeated digestion of the same sample, the portion in solution being richer in silica than the original clay.<sup>1</sup> In dilute acids<sup>2</sup> of the proper concentration (0.1 to 0.4 percent), bases and silica go into solution in the same proportion as in the original clay. In dilute alkalies<sup>3</sup> maximum silica is removed at about one-tenth (0.02 percent) that concentration of alkali. Clays such as the well-known swelling bentonite of Wyoming, which are sodium-saturated to nearly base-exchange capacity, dissolve rather freely in water.

In the present investigation the solubilities of a variety of montmorillonites were determined in dilute acid solutions of a wide range of concentration in order

to determine possible equilibrium relations between the four components—silica, bases, water, and acid—with clay in excess. Silica and bases were determined in the solids recovered from the filtrate by evaporation. The state of bases and silica in solution was further investigated by electrodialysis. The next step in this research is the synthesis of clays by combining bases and silica (both in solution) with water and free acid in varying proportions.

The experimental procedure was to put 30 grams of ground clay in a 2-liter flask, fill with distilled water, add acid or alkali to the desired concentration, then digest for 48 hours at 90° C. on an electric stove. The usual series of concentrations was 0.02, 0.04, 0.1, 0.2 to 4 percent with interpolations in the critical regions between 0.2 and 1 percent and others between 0.0 and 0.02. Repeated runs showed satisfactory duplication. Higher precision would require thermostatic control of digestion and filtration temperatures.

Each filtrate was evaporated down to 150 milliliters, placed in a weighed pyrex beaker, then brought to dryness at 160° C. and weighed. The water-soluble salts were next removed with hot distilled water, the residue brought to 160° and again weighed. A final digestion in hot strong acid separated silica and bases. Water-soluble and water-insoluble bases were separately determined. Special tests indicated that little or no  $R_2O_3$  was insolubilized by drying, probably because free acid is always present.

A set of preliminary tests on 22 related clays, each in 2 liters of 0.2 percent hydrochloric acid, gave without exception a light-brown water-insoluble residuum. A typical residue analyzed by R. E. Stevens, of the Geological Survey, had the composition of montmorillonite. A thermal analysis gave a weight-temperature curve similar to that of montmorillonite but lacking the shoulder at 500° C. indicative of lattice water. These residues were, of course, isotropic and remained so for months. Such substances as bentonites, fuller's earths, glauconites, decomposed granites, and garden soil all gave 1 to 2 grams of residue. Pyrophyllite, bauxites, and tuffs gave only about half a gram. Other experiments showed the effect of added chlorides (aluminum, iron, magnesium, calcium) to beslight, but added silica solution gave an enhanced yield of bases.

<sup>1</sup> Nutting, P. G., *Solution and dispersion of minerals in water*: Washington Acad. Sci. Jour., vol. 22, p. 261-267, 1932.

<sup>2</sup> Nutting, P. G., *a study of bleach clay solubility*: Franklin Inst. Jour., vol. 224, pp. 339-362, 1937.

<sup>3</sup> *Idem*, pp. 359.



The gist of the problem is then to find relations between (1) the ions in solution, (2) the hydrosols carrying ionic atmospheres, and (3) the bases contained in the aluminosilicate clay structure. In the present series of experiments the clay was always in excess, but with clay limited to one or two grams per liter the picture is quite different.<sup>4</sup> With clay limited and an excess of solvent solution, a fraction of the clay is always left undissolved. This is a further indication that the equilibrium established is a reversible one.

#### SOLUBILITY OF SILICA

At each temperature, opaline silica has a perfectly definite solubility or dispersibility in water. The state of the hydrosol in solution or dispersion is not definitely known, but the micellae must be very small, because even a saturated solution or dispersion is readily filterable and dialyzable. The silica itself is not ionized, but the particles appear to carry adsorbed hydrogen and hydroxyl charges in equal proportion, as shown by electrodialysis. The hydrosol particles appear to vary little in size or character in any one solution up to ten times supersaturation.

A silica solution may be made highly supersaturated by evaporation in pyrex or metal vessels if all solid particles are removed from it by filtration. At 10- to 20-fold saturation the solution becomes cloudy, and at 40- to 60-fold saturation the hydrosol turns to a gel. Silica hydrosol, like a gelatin solution or a clay suspension, will lose water in a saturated atmosphere until its water content is about 44 percent ( $\text{Si}_2\text{O} \cdot 2.5\text{H}_2\text{O}$ ). In an atmosphere free from water vapor it will dry at room temperature until its water content is about 12 percent. At 100° C. its weight is about 1.10 times base weight at 950° C., at 500° about 1.05 times, and at 800° about 1.02 times, the slope of the weight-temperature curve being fairly uniform from 120° to 940° C. Silica gel holds more water at 700° C. than even such well-formed silicate structures as those of talc and pyrophyllite. At lower temperatures, therefore, silica gel is an indefinite mixture of hydrates or silicic acids.

The solubility of opaline silica in water has been carefully determined by Lenher and Merrill<sup>5</sup> at 25° and 90° C. and by Hitchen<sup>6</sup> at 13 higher temperatures up to 336° C., using a specially designed autoclave. Their values agree well with each other and with many less precise determinations of my own and form a smooth curve from which are taken the values given in table 1 and plotted in figure 23. The uncertainty in these values of solubility is probably less than 2 percent. If greater precision is required, attention should perhaps

first be given to the temperature range 50° to 150° C. and to avoiding supersaturation.

TABLE 1.—*Solubility of opaline silica in water*

Temperature (°C.)	Silica (parts per million)	Variation per degree centigrade	Temperature (°C.)	Silica (parts per million)	Variation per degree centigrade
0-----	106	3. 10	200-----	915	5. 8
25-----	185	3. 20	250-----	1250	7. 5
50-----	270	3. 34	300-----	1700	10. 5
100-----	445	3. 80	350-----	2400	19. 0
150-----	650	4. 5			

Of chief interest here are the factors which influence solubility. Dilute acids (0 to 0.5 percent) dissolve precisely the same amount of silica as pure water, strong acids (6 to 20 percent) dissolve less. The removal of hydrogen and hydroxyl ions from the silica micellae causes them to flocculate and precipitate. Strong solutions of acids and of many salts, as well as electrodialysis, have this effect on hydrosols, an effect similar to plasmolysis in biology. A silica solution supersaturated as much as ten times (2 grams per liter) may be kept at room temperature for years in good bottles or pyrex glass without any precipitation of silica if no particles of solid silica are present. With solid silica present, the concentration will drop to saturation in a few days; with certain clays present, it will drop in a few hours.

The solubility of silica gel in acids of different concentrations at 90° C. was determined by Lenher and Merrill.<sup>7</sup> Their values for hydrochloric acid are given in table 2 and figure 24.

TABLE 2.—*Solubility of silica in hydrochloric acid solutions*

Strength of acid (percent)	Silica dissolved (grams per liter)	Strength of acid (percent)	Silica dissolved (grams per liter)
0.0-----	0. 418	7.6-----	0. 230
1.2-----	. 408	9.3-----	. 190
3.0-----	. 374	10.0-----	. 182
3.8-----	. 354	13.6-----	. 112
5.3-----	. 302	15.8-----	. 088
6.3-----	. 268	18.6-----	. 058

Solubility zero is indicated for about 24 percent acid. The plotted curve is slightly S-shaped rather than linear. Plotting log solubility against log acid concentration gives a curve of steadily increasing slope, hence the effect of the acid increases continuously as regards energy of solution. Evidently the silica being dissolved is less and less hydrated as the acid concentration is increased, the hydrochloric acid and silica micellae competing for the water. The effect here noted doubtless has a bearing on the commercial activation of bentonites where 20 percent acid is used.

<sup>4</sup> Idem, p. 359.

<sup>5</sup> Lenher, V., and Merrill, H. B., The solubility of silica: Am. Chem. Soc. Jour., vol. 39, p. 2630, 1917.

<sup>6</sup> Hitchen, C. S., A method for the experimental determination of hydrothermal solutions, with notes on its application to the solubility of silica: Inst. Min. Met. Bull., vol. 364, pp. 1-26, 1935.

<sup>7</sup> Lenher, V., and Merrill, H. B., op. cit., p. 2636.

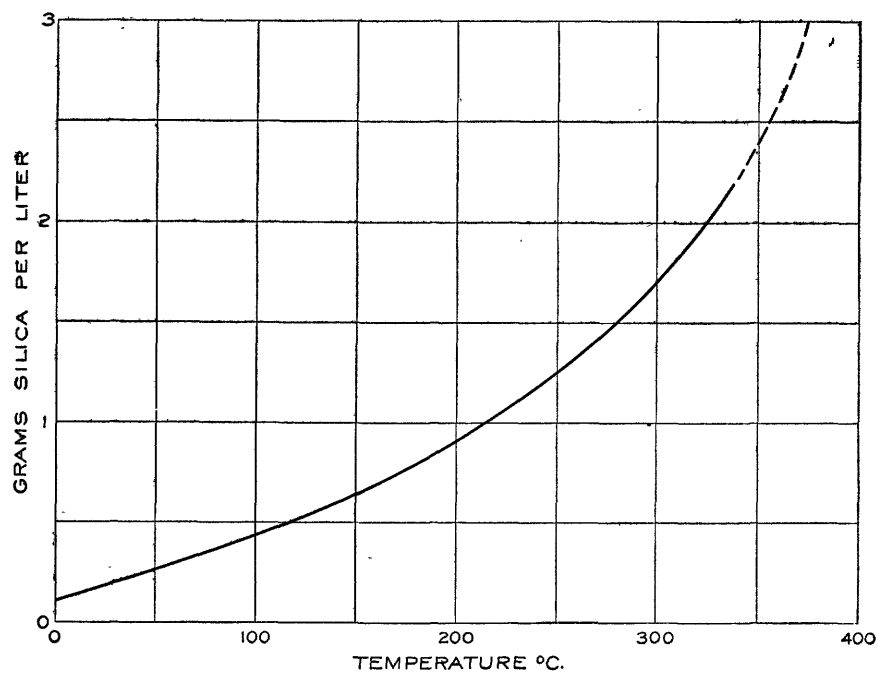


FIGURE 23.—Solubility of opaline silica in water at different temperatures (after Hitchen).

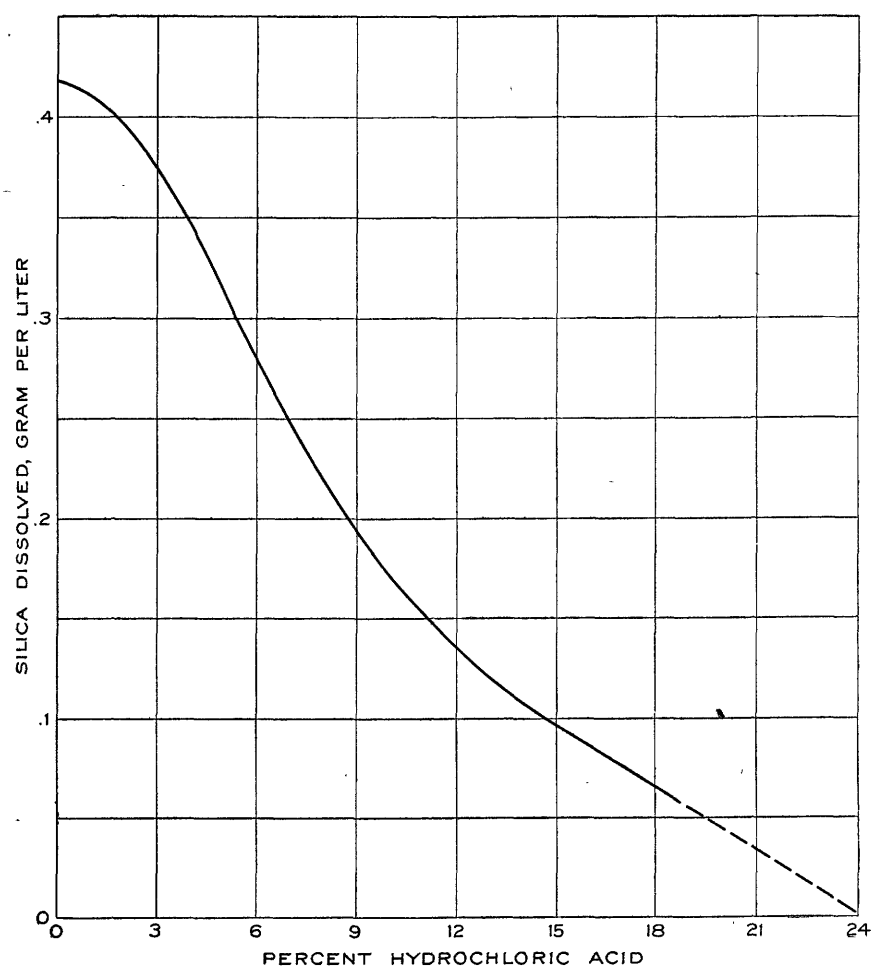


FIGURE 24.—Solubility of silica in hydrochloric acid solutions.

Very different in their effect on the solubility of silica are the hydrates and salts of such bases (sodium, potassium, magnesium) as combine with silicic acid to form silicates. Each base has its own specific behavior and its effect varies also with concentration, with acidity, with temperature, and with age. Even electro dialysis fails to disclose all the details of the effect of an added salt. Sodium chloride promotes the transport of silica as cations, aluminum chloride as anions, yet a solution of sodium silicate gives equal transport of silica as anions and cations. A silica gel containing a little sodium silicate cannot be freed from sodium by washing in water; the sodium must first be converted to another salt.

Factors affecting the solution or dispersion of silica in water may then be thus roughly classified:

1. Adsorbable ions, nonsilicate forming. Effect nil in low concentrations, solubility depressing at high.
2. Cations capable of forming soluble silicates. These assist more silica into solution.
3. Cations forming insoluble silicates. These do not affect the limiting saturation.

Substances loosely called "mineralizers" by geologists may fall in any of these three classes but perhaps

more commonly in the third. Hitchen<sup>8</sup> defines them as substances which inhibit the formation of structureless aggregates and thus promote crystallization.

#### SOLUBILITY OF MONTMORILLONITE CLAYS IN ACID SOLUTIONS

The six clays selected for study represent different types commonly met with, ranging from the alkaline swelling variety to the Japanese acid clay. The Polkville clay is the purest montmorillonite bentonite now known. The Quincy clay is a selected fuller's earth of high purity, but it differs slightly from ordinary montmorillonite in its optical properties and in its weight-temperature curve. Soil was included in order to compare the behavior of its soluble constituents, thought to be chiefly montmorillonite, with those of pure bentonites. Filtrol, an acid-activated Arizona bentonite, showed the effect of the preliminary removal of about half its bases. All filtrates became hydrogel when their concentration reached about 1 gram per 20 milliliters. Total and water-insoluble residues were weighed after heating to 160°,  $R_2O_3$  and silica after ignition. The data, given in grams per liter of solution, are summarized in tables 3 to 8.

<sup>8</sup> Hitchen, C. S., A method for the experimental investigation of hydrothermal solutions, with notes on its application to the solubility of silica, author's reply to discussion: Inst. Min. Met. Bull. 375, p. 27, 1935.

TABLE 3.—Total residue

Percent acid.....	0.0	0.02	0.04	0.10	0.2	0.4	1.0	2.0	4.0
Wyoming clay:									
Hydrochloric acid.....	0.405	0.433	1.031	1.675	1.900	3.21	3.58	5.61	8.30
Sulphuric acid.....	.405	.521	.545	.680	.872	1.25	2.35	6.95	-----
Oxalic acid.....	.405	.522	1.120	1.448	1.987	4.63	6.53	-----	-----
Japanese clay, hydrochloric acid.....	.073	.294	.478	.684	.771	1.30	2.54	2.82	-----
Polkville clay, hydrochloric acid.....	{ .042 } .021	.344	.520	.777	1.264	2.15	4.28	8.83	-----
Quincy clay, hydrochloric acid.....	.080	.568	.960	1.483	1.903	1.98	3.16	5.25	11.20
Soil, hydrochloric acid.....	.117	.342	.453	.829	1.263	2.25	2.90	5.36	-----
Filtrol, hydrochloric acid.....	.717	-----	.842	1.237	1.408	2.25	7.67	10.53	-----

TABLE 4.—Water-soluble part of residue

Percent acid.....	0.0	0.02	0.04	0.10	0.20	0.4	1.0	2.0	4.0
Wyoming clay, hydrochloric acid.....	0.312	0.347	0.716	1.063	1.055	1.58	2.02	3.90	6.19
Japanese clay, hydrochloric acid.....	None	.198	.293	.231	.303	.491	.651	.692	-----
Polkville clay, hydrochloric acid.....	{ .017 } .015	.240	.369	.552	.740	1.176	3.42	8.05	-----
Quincy clay, hydrochloric acid.....	.023	.287	.574	.886	.966	.934	2.11	4.27	10.64
Soil, hydrochloric acid.....	.074	.212	.298	.498	.782	1.720	1.83	4.22	-----
Filtrol, hydrochloric acid.....	.313	-----	.304	.411	.464	.725	6.12	8.90	-----



TABLE 5.—*Water-insoluble residue (silicates, etc.)*

Percent acid .....	0. 0	0. 02	0. 04	0. 1	0. 2	0. 3	0. 4	0. 6	1. 0	2. 0	4. 0
Wyoming clay:											
Hydrochloric acid.....	0. 093	0. 086	0. 315	0. 612	0. 845	1. 289	1. 64	1. 71	1. 57	1. 70	2. 11
Sulphuric acid.....	. 093	. 080	. 158	. 226	. 251	. 573	. 869	. 950	. 971	. 917	1. 30
Oxalic acid.....	. 093	. 264	. 620	. 621	. 933	1. 120	1. 156	1. 149	1. 11	-----	-----
Japanese clay, hydrochloric acid.....	. 073	. 096	. 185	. 454	. 468	. 799	. 806	. 797	1. 89	2. 13	-----
Polkville, clay, hydrochloric acid.....	{ . 025 . 006 }	. 104	. 152	. 325	. 524	. 810	. 971	1. 025	. 860	. 775	-----
Quincy clay, hydrochloric acid.....	. 057	. 281	. 386	. 597	. 937	1. 035	1. 050	1. 062	1. 049	. 987	. 566
Soil, hydrochloric acid.....	. 043	. 130	. 156	. 331	. 481	. 545	. 532	. 689	1. 062	1. 141	-----
Filtrol, hydrochloric acid.....	. 404	. 486	. 538	. 826	. 944	1. 430	1. 524	1. 545	1. 55	1. 63	-----

TABLE 6.—*Silica dissolved*

Percent acid .....	0. 0	0. 02	0. 04	0. 1	0. 2	0. 3	0. 4	0. 6	1. 0	2. 0	4. 0
Wyoming clay:											
Hydrochloric acid.....	0. 064	0. 049	0. 198	0. 378	0. 461	0. 808	0. 885	0. 744	0. 662	0. 877	0. 957
Sulphuric acid.....	. 064	. 070	. 138	. 204	. 232	. 406	. 747	. 958	. 971	. 917	-----
Oxalic acid.....	. 064	. 188	. 446	. 551	. 933	1. 100	1. 156	1. 110	. 896	-----	-----
Japanese clay, hydrochloric acid.....	. 053	. 082	. 136	. 239	. 275	. 332	. 459	. 522	. 558	. 634	-----
Polkville clay, hydrochloric acid.....	{ . 024 . 010 }	. 084	. 140	. 244	. 361	. 558	. 664	. 695	. 668	. 618	-----
Quincy clay, hydrochloric acid.....	. 050	. 169	. 300	. 434	. 557	. 573	. 580	. 579	. 559	. 354	. 206
Soil, hydrochloric acid.....	. 018	. 038	. 066	. 149	. 232	. 268	. 290	. 421	. 563	. 504	-----
Filtrol, hydrochloric acid.....	. 353	. 358	. 328	. 430	. 464	. 556	. 594	. 574	. 549	. 491	-----

TABLE 7.—*R<sub>2</sub>O<sub>3</sub> from water-soluble salts (chlorides, etc.)*

Percent acid.....	0. 0	0. 02	0. 04	0. 1	0. 2	0. 3	0. 4	0. 6	1. 0	2. 0	4. 0
Wyoming clay:											
Hydrochloric acid.....	None	None	None	0. 022	0. 082	0. 126	0. 150	0. 219	0. 333	0. 730	1. 891
Oxalic acid.....	None	None	0. 010	. 205	. 695	. 658	. 598	. 652	. 781	-----	-----
Japanese clay, hydrochloric acid.....	None	0. 031	. 064	. 039	. 034	. 075	. 106	. 115	. 117	. 300	-----
Polkville clay, hydrochloric acid.....	None	None	. 012	. 015	. 034	. 144	. 161	. 148	. 109	2. 292	-----
Quincy clay, hydrochloric acid.....	None	. 027	. 042	. 158	. 183	. 179	. 172	. 173	. 546	1. 300	3. 540
Soil, hydrochloric acid.....	None	. 051	. 071	. 146	. 269	. 480	. 637	. 995	1. 123	1. 158	-----
Filtrol, hydrochloric acid.....	0. 010	. 041	None	None	. 021	. 024	. 026	. 120	1. 598	2. 650	-----

TABLE 8.—*R<sub>2</sub>O<sub>3</sub> from water-insoluble salts (silicates, etc.)*

Percent acid.....	0. 0	0. 02	0. 04	0. 1	0. 2	0. 3	0. 4	0. 6	1. 0	2. 0	4. 0
Wyoming clay:											
Hydrochloric acid.....	None	None	None	0. 042	0. 146	0. 290	0. 362	0. 432	0. 391	0. 469	0. 779
Oxalic acid.....	None	0. 031	0. 142	. 071	None	None	None	. 051	. 212	-----	-----
Japanese clay, hydrochloric acid.....	0. 002	. 015	. 019	. 116	. 094	. 135	. 185	. 370	. 730	. 622	-----
Polkville clay, hydrochloric acid.....	None	None	None	. 027	. 092	. 174	. 209	. 216	. 174	. 065	-----
Quincy clay, hydrochloric acid.....	None	. 068	. 034	. 084	. 239	. 302	. 313	. 298	. 339	. 406	. 266
Soil, hydrochloric acid.....	None	. 025	. 034	. 101	. 149	. 125	. 113	. 145	. 287	. 333	-----
Filtrol, hydrochloric acid.....	None	None	. 032	. 099	. 192	. 350	. 442	. 481	. 517	. 649	-----

## DISCUSSION OF DATA

In these clays the silica ranges from 70 to 76 percent on a water-free basis. For comparison there have been computed (1) the silica fraction in the water-

insoluble residue, (2) the ratio of silica to  $\text{SiO}_2 + \text{R}_2\text{O}_3$  in the residue (clay formed?), and (3) the ratio of silica to total  $\text{R}_2\text{O}_3$  in the original solution (clay dissolved?). These are given in tables 9 to 11,

TABLE 9.—*Silica fraction of the water-insoluble material*

Percent acid.....	0	0.02	0.04	0.1	0.2	0.3	0.4	0.6	1.0	2.0	4.0
Wyoming clay:											
Hydrochloric acid.....	0.688	0.563	0.629	0.618	0.546	0.627	0.540	0.435	0.422	0.522	0.454
Oxalic acid.....	.688	.764	.719	.887	1.000	1.000	1.000	.966	.807	-----	-----
Japanese clay, hydrochloric acid.....	.727	.848	.735	.526	.588	.416	.569	.655	.295	.283	-----
Polkville clay, hydrochloric acid.....	.933	.808	.921	.751	.679	.689	.684	.678	.777	.797	-----
Quincy clay, hydrochloric acid.....	.872	.603	.777	.727	.594	.554	.442	.546	.533	.359	.417
Soil, hydrochloric acid.....	.429	.292	.423	.450	.482	.492	.545	.611	.530	.442	-----
Filtrol, hydrochloric acid.....	.874	.736	.610	.521	.492	.389	.390	.372	.354	.301	-----

TABLE 10.—*Ratio of silica to  $\text{SiO}_2$  + water-insoluble  $\text{R}_2\text{O}_3$* 

Percent acid.....	0	0.02	0.04	0.1	0.2	0.3	0.4	0.6	1.0	2.0	4.0
Wyoming clay:											
Hydrochloric acid.....	1.000	1.000	1.000	0.900	0.759	0.736	0.710	0.633	0.629	0.652	0.551
Oxalic acid.....	1.000	.858	.759	.886	1.000	1.000	1.000	.956	.809	-----	-----
Japanese clay, hydrochloric acid.....	.996	.845	.877	.673	.745	.711	.486	-----	.433	.489	-----
Polkville clay, hydrochloric acid.....	1.000	1.000	1.000	.900	.797	.762	.761	.763	.793	.905	-----
Quincy clay, hydrochloric acid.....	1.000	.713	.898	.838	.700	.655	.649	.660	.622	.496	.470
Soil, hydrochloric acid.....	1.000	.603	.660	.596	.609	.682	.720	.744	.662	.602	-----
Filtrol, hydrochloric acid.....	1.000	1.000	.911	.813	.707	.614	.573	.544	.515	.431	-----

TABLE 11.—*Ratio of silica to  $\text{SiO}_2$  + total  $\text{R}_2\text{O}_3$* 

Percent acid.....	0	0.02	0.04	0.1	0.2	0.3	0.4	0.6	1.0	2.0	4.0
Wyoming clay:											
Hydrochloric acid.....	1.000	1.000	1.000	0.855	0.669	0.660	0.634	0.533	0.478	0.422	0.264
Oxalic acid.....	1.000	.858	.746	.666	.573	.626	.659	.612	.474	-----	-----
Japanese clay, hydrochloric acid.....	.964	.639	.621	.607	.682	.613	.612	.518	.397	.407	-----
Polkville clay, hydrochloric acid.....	1.000	1.000	.921	.853	.741	.637	.642	.656	.702	.208	-----
Quincy clay, hydrochloric acid.....	1.000	.641	.798	.642	.569	.544	.545	.551	.387	.172	.058
Soil, hydrochloric acid.....	1.000	.333	.386	.376	.357	.303	.279	.270	.285	.253	-----
Filtrol, hydrochloric acid.....	.972	.897	.911	.813	.685	.598	.559	.489	.206	.130	-----

Water and very dilute acids tend to dissolve excess silica, but the residues from the stronger acid solutions (1 to 4 percent) are deficient in silica. Soil departs from this rule, organic matter apparently lowering the solubility of silica at the lower acid concentrations. Each series of residues bears no simple relation to the acid present (nor is this the case with alkaline solutions) and they must be represented graphically to show significant details.

The solubility of silica (shown in fig. 25) is slightly lower for 0.02 percent acid (0.0486 gram per liter) than for pure water (0.0641), the silica of sodium silicate being insolubilized by the acid. This bentonite contains about 2.5 percent  $\text{Na}_2\text{O}$ . From 0.02 to about 0.2 percent acid the solubility increases steadily, jumps to a maximum (0.8859 gram per liter) at 0.4 percent, drops to a minimum (0.662) at 1 percent, then rises again to 0.957 at 4 percent. The release of sesquioxides begins at about 0.05 percent acid. Water-soluble  $\text{R}_2\text{O}_3$  (as  $\text{RCl}_3$ ) increases regularly. The graph of water-insoluble  $\text{R}_2\text{O}_3$  is similar to that for silica, but with points of

inflexion displaced toward higher concentration.

The silica released by oxalic acid (see fig. 26) is considerably greater in quantity than that released by hydrochloric acid; but the graphs show similar trends. The sesquioxides however behave very differently. The water-soluble salts (oxalates) show a pronounced maximum (at 0.2 percent) and minimum (at 0.4 percent acid). The recombined  $\text{R}_2\text{O}_3$ , after rising to 0.142 gram per liter at 0.04 percent, drops to zero at 0.2 to 0.4 percent, then rises steeply. This loss of power to recombine through a range of acid concentrations was not found with any other acid or clay.

The silica removed from the Japanese acid clay (see fig. 27) increases from the start (in pure water 0.0529 gram per liter, in 0.02 percent acid 0.0816 gram per liter) but at a varying rate. A critical acid concentration between 0.2 and 0.3 percent is indicated for even this clay. The curves for both soluble and insoluble  $\text{R}_2\text{O}_3$  are irregular. The excess of insoluble (silicate)  $\text{R}_2\text{O}_3$  over silica (0.730 to 0.558 gram) at about 1 percent acid is noteworthy.

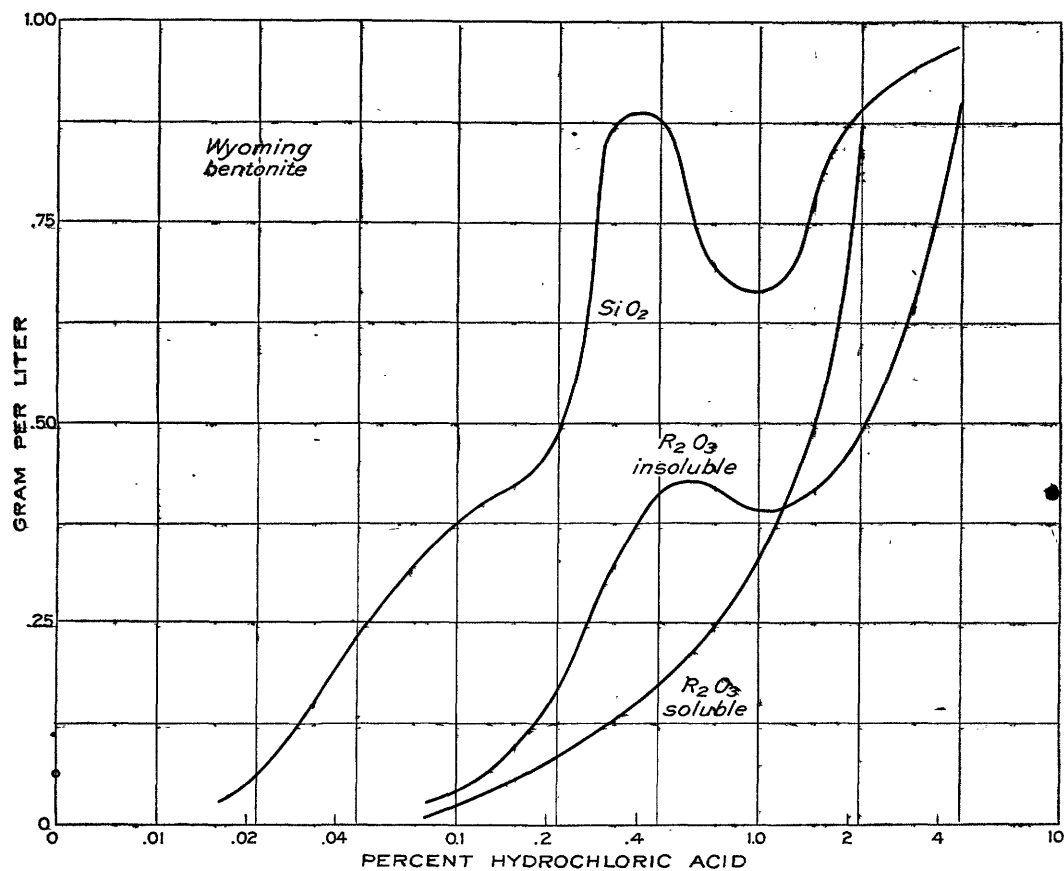


FIGURE 25.—Wyoming bentonite in hydrochloric acid solutions.

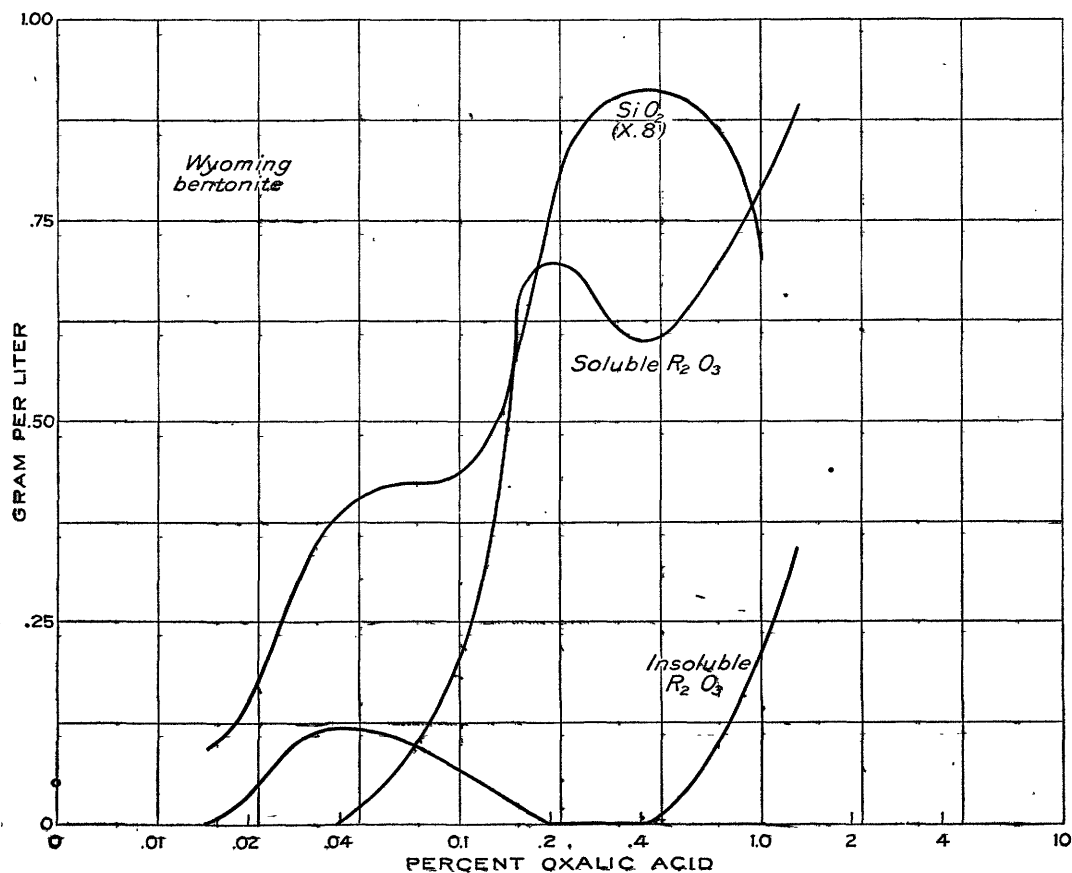


FIGURE 26.—Wyoming bentonite in oxalic acid solutions.

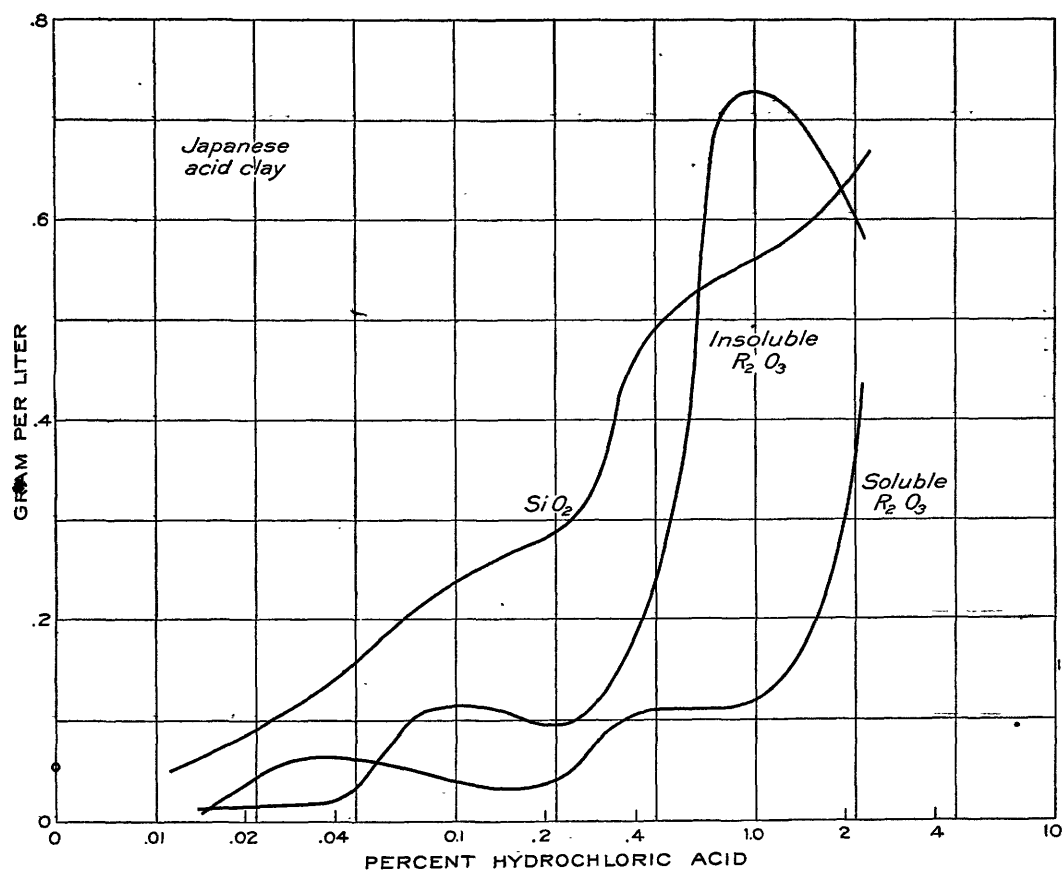


FIGURE 27.—Japanese acid clay in hydrochloric acid solutions.

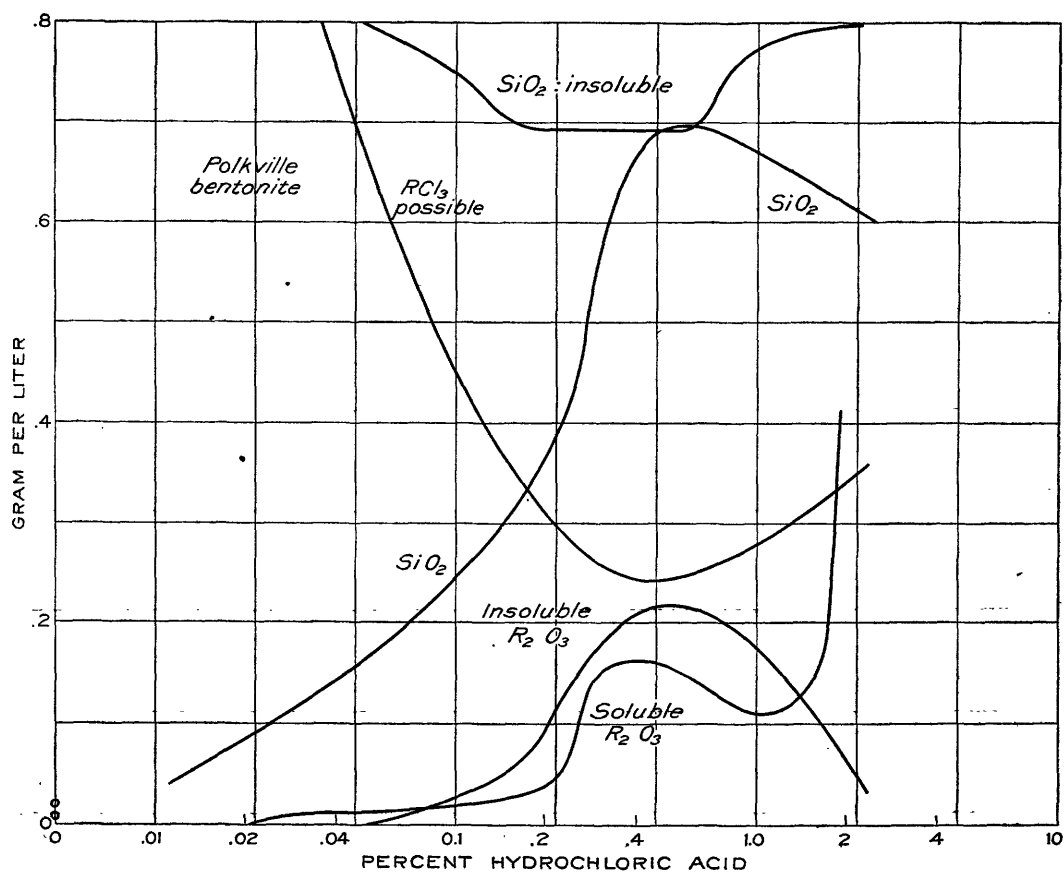


FIGURE 28.—Polkville bentonite in hydrochloric acid solutions.

The solubility curves (fig. 28) for the Polkville bentonite, a very pure montmorillonite, are simple and may be regarded as standard for this type of material. No secondary effects due to minor impurities are apparent. The silica dissolved in pure water is very low, 0.0236 gram per liter for first run and only 0.0102 for a second run on the same material. With 0.02 percent acid it is 0.0816 gram per liter, and it rises steadily to normal (0.42 gram per liter at 90°) at about 0.23 percent, then rises steeply to a high broad maximum of about 0.7 gram per liter. Recombined  $R_2O_3$  rises to a similar broad maximum at about the same concentration of acid, but is zero at concentrations below about 0.04 percent acid, and is small or zero above about 3 percent acid. Silica in the recombined material is in the same proportion as in montmorillonite over the range 0.25 to 0.7 percent acid, and is higher than normal above and below this range. Above 2 percent acid the silica hydrosol is unable to withhold much  $R_2O_3$  against solution in acid, although at 0.5 percent its retarding effect is a maximum. Of the dissolved material, a part (chiefly  $RCl_3$ ) is water-soluble after drying at 160° C. Taking the ratio of this to the maximum possible aluminum chloride computed from the acid present gives a curve dropping from 0.983 at 0.02 percent acid to a minimum 0.241 at 0.4 percent acid, then rising again at higher concentrations, thus checking closely with the silica and silicate  $R_2O_3$  curves. Of 1.5 grams of this clay digested in 2 liters of 0.3 percent hydrochloric acid, 22.5 percent remained undissolved after 48 hours, the residue closely resembling the original clay.

The shift of equilibrium produced by a large reduction in concentration was investigated on this Polkville bentonite. About 4 grams was digested in 100 milliliters of 20 percent hydrochloric acid until all bases were in solution, leaving pure white silica. Then solution and silica were dumped into two liters of water at 90° and left for 5 days to come to a new equilibrium. The question was whether the silica would take up bases or the bases in solution take up silica to form montmorillonite in equilibrium with such a solution. On filtering and analyzing, no bases were found with the solid silica (less than 0.1 percent left by hydrofluoric acid). In the evaporated filtrate were found the normal amounts of water-soluble and insoluble residue, that is, water-insoluble  $R_2O_3$ , 0.1789 gram per liter, and  $SiO_2$  0.1481 gram per liter, equivalent to 45.3 percent. An electro-dialysis of 600 milliliters of the final solution gave for silica as cations 55.7 percent, as anions 44.3 percent, while the  $R_2O_3$  as cations was 75.0 percent, as anions 25.0 percent. In another test, dissolved bases (slightly acid), dissolved silica, and water were combined in proportion to synthesize a clay, then a few grams of pure dry silica was added. In this case the bases nearly all went to the solid silica, some were left in solution after sufficient acid had been set free to keep them in

solution. With neither pure acid nor solid silica present some of the trivalent bases hydrolyze and precipitate, releasing acid.

The Quincy clay used in the tests was selected natural rock from the Hawthorn formation of Miocene age, in northwest Florida, the purest and highest grade of fuller's earth known. A thin section shows it to be all or nearly all crystalline material, of which large aggregates have little orientation. Its thermal dehydration curve differs widely from those of known pure montmorillonite, such as the Polkville clay, and there is some doubt as to the nature of the dominant mineral. Chemical analyses and the solubility curves (fig. 29) tell little on this point. Of 1.5 grams of this clay digested 48 hours in 2,000 milliliters of 0.3 percent hydrochloric acid 16.2 percent remained undissolved.

The silica dissolved from this clay varies like that dissolved from the pure bentonite (Polkville clay), but the maximum is broader and the solubility is twice as high in 0.02, 0.04, and 0.1 percent acid. On account of the high solubility in 0.02 percent acid, extra points were determined at 0.004 and 0.01 percent acid to show the nature of the approach to solubility in pure water. Recombined  $R_2O_3$  shows three maxima at 0.02, 0.4, and 1.8 percent acid. Water soluble  $R_2O_3$  starts at about 0.01 percent and shoots up at 1 percent acid.

In testing soil the material used was that part of a good garden soil that could be put through a 150-mesh sieve by rubbing without grinding. It was essentially well decomposed rock with abundant humus and some exchangeable lime. The solubility in pure water is low (see fig. 30) and rises but little in very dilute acids. The solubility of silica rises above that in pure water between 0.6 and 3 percent acid, with a maximum at 1 percent. Recombined  $R_2O_3$  has two maxima at 0.2 and 1.6 percent acid. Water-soluble  $R_2O_3$  (as  $RCl_3$ ) rises steeply above 0.2 percent acid. Organic matter interfered, but the three curves indicate that soil fines behave toward dilute acids essentially like montmorillonite.

Commercial "filtrol," a bentonite from Chambers, Ariz., previously activated by removal of about half its bases in 20 percent acid, was used in this test. It is of interest in showing the effect of this pretreatment on the solubility. In pure water and in acid solutions up to 0.1 percent acid the silica solubility (see fig. 31) is just below that of silica gel (0.420 gram per liter at 90°), but from 0.1 percent to 4 percent acid it is higher. Recombined  $R_2O_3$  indicates the usual critical region at about 0.3 percent acid. All the dissolved  $R_2O_3$  is recombined in the range 0.04 to 0.1 percent, and the uncombined  $R_2O_3$  is very low over the whole range from 0 to 0.4 percent acid. At higher acid concentrations, however, it shoots up. This clay exhibits the usual critical range, 0.2 to 0.4 percent acid, and is unusual only in its high silica solubility and in the nearly complete recombination of  $R_2O_3$  in solution.

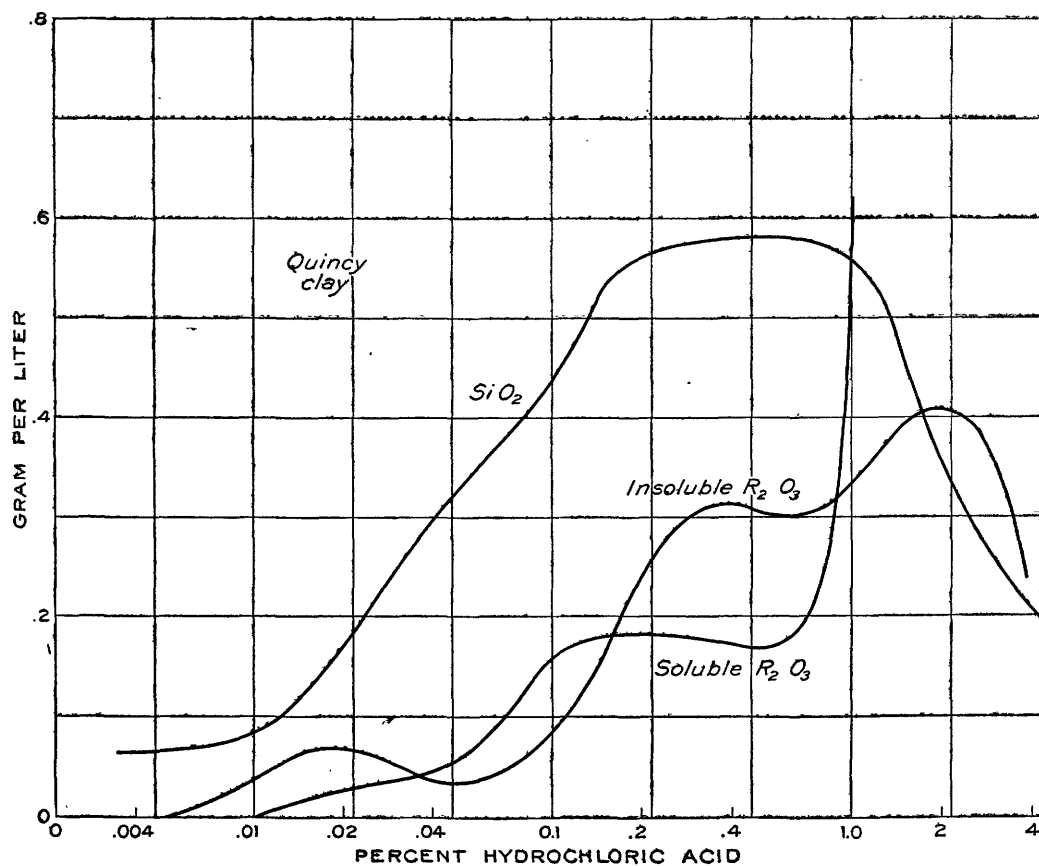


FIGURE 29.—Quincy clay (Florida fuller's earth) in hydrochloric acid solutions.

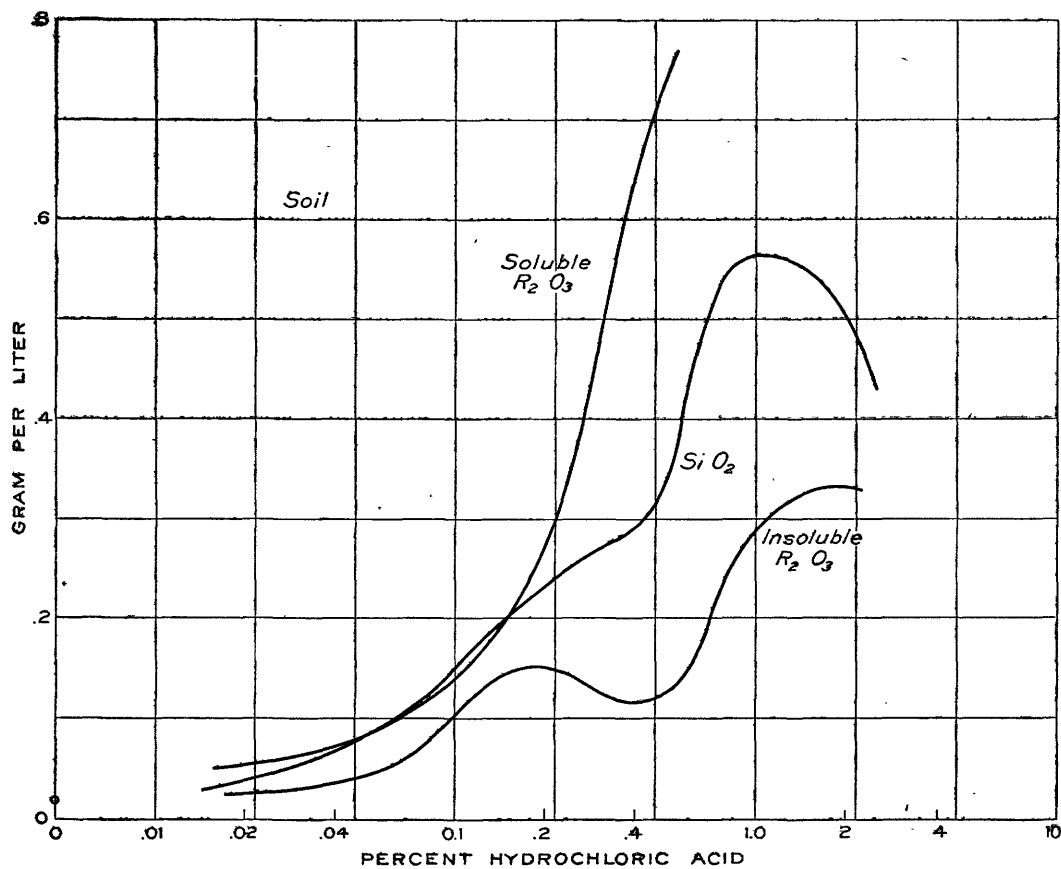


FIGURE 30.—Soil in hydrochloric acid solutions.



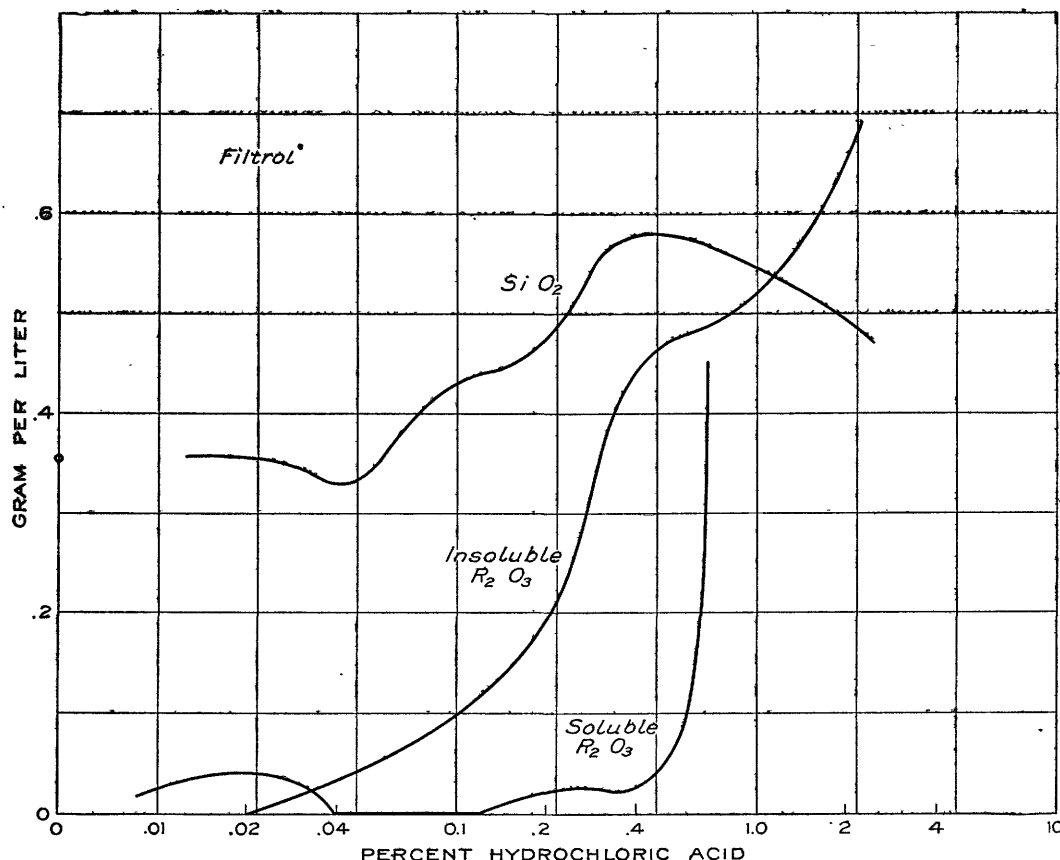


FIGURE 31.—Filtrol (activated bentonite) in hydrochloric acid solutions.

## INTERPRETATION OF DATA

The system to be considered is one of at least five components—montmorillonite (in excess), water, free acid, chlorides in solution, and hydrosols in suspension—brought to equilibrium by a 48-hour digestion at 90° C. The montmorillonite is finely crystalline with a definite structure and narrow range of composition. Its bases are readily removed by acids, leaving amorphous silica readily soluble in water at 90° up to 0.420 gram per liter. Silica in solution is not ionized to any appreciable extent, if at all, but is hydrated. It probably exists as micellae of 1,000 or more molecules in each aggregate, but these are submicroscopic and filterable. Although not itself ionized, a silica micella has the unusual property of attracting other ions to itself and holding them either fixed on its surface or under restraint in its osmotic atmosphere. If the micella is forcibly stripped of these ions, the silica floculates and precipitates as gel. In addition to the just-mentioned three forms of water associated with silica—free water, ionized H and OH and osmotic, and adsorbed water—there is doubtless a fourth, familiar to biologists, namely intermicellar H and OH, which differs from the osmotic water in that the ions are free to wander within the confines of the micellar group.

Basic ions are drawn into solution by the free acid and out of solution by the clay and by the silica hydro-

sol. With removal of free acid, bases revert to the silica. Chloride and silicate ions compete for the bases, whereas hydrogen ions compete with other cations for anions. In either effect the law of mass action applies, each being reversible.

The curves of figures 25 to 31 check well with such an interpretation. It is only after silica has approached saturation (0.42 gram per liter) that combined  $R_2O_3$  rises sharply. At the lowest concentrations of acid it is chiefly the ions of water that are active in dissolving clay and reforming silicate in solution. With increasing acid, the ratio of H (or  $H_2O$ ) to Al adsorbed on the hydrosol decreases steadily from nearly unity to nearly zero. Within the critical range of acid concentrations (silica in solution exceeding saturation)  $R_2O_3$  combines with the silica in solution in such a manner as to withdraw it from competition with the uncombined silica for the water, probably as montmorillonite in composition though not in structure. This is shown clearly by the upper curve in figure 28,  $SiO_2:(SiO_2+R_2O_3)$ . With high acid concentrations (2 to 20 percent), excess hydrogen is again available, the solubility of silica drops, and acid anions are again able to hold bases from union with silica. The ratio of soluble salts to total acid shown in figure 28 also checks with this conclusion. That ratio is a minimum over the critical range.

With low and increasing concentrations of acid the silicate hydrosol ranges from the pure hydrate silicic acid as end member up to the composition of montmorillonite, the ratio of hydrogen to aluminum dropping steadily. It should be possible to compute an equilibrium constant but that the amount of free acid is unknown and the various bases present are not adiabatically interchangeable. The curves of figures 25 to 31 are plotted as mass against log concentration of acid. Horizontal portions of these curves (maxima and minima) indicate no net work done by acid of that concentration. At a silica maximum, silica goes from clay to hydrosol without assistance from acid. With the Japanese clay (figure 27) assistance, possibly in breaking down structure, is required at all concentrations. With the alkaline Wyoming clay (fig. 25), the slope is reversed between 0.4 and 1 percent acid, the interpretation being perhaps that silica is unable to compete with free acid for the bases in this range. When the curve for recombined  $R_2O_3$  is horizontal, evidently acid and hydrosol are stalemated for possession of the bases. With the Quincy clay (fig. 29) there are three such maxima but two of these may perhaps be attributed to hydrates in the clay.

Calcium is a minor constituent in all these clays but was determined in each solution. It has not been mentioned because it evidently plays a minor role. From the four pure montmorillonite clays it is not removed, more than a trace, by pure water. It appears in the most dilute acid solutions, accounting for about one-fourth of the acid. It increases in proportion to the acid up to about 0.1 percent of acid, reaching a value that is constant for higher acid concentrations. Soil and acid-treated filtrol give up calcium even to pure water (5 and 75 milligrams, respectively, per liter), and with 0.02 percent or more of acid the calcium in solution remains constant (28 and 130 milligrams). Magnesium was not regularly determined, as it was found in but few solutions in barely measurable amounts.

#### SOLUBILITY OF MONTMORILLONITE CLAYS IN ALKALINE SOLUTIONS

As with acid solutions, 30 grams of montmorillonite clay was digested 48 hours at 90° in 2-liter solutions of sodium carbonate of different concentrations. The filtered solution was acidified during evaporation, the residue was washed in hot distilled water and silica determined. There was no RO or  $R_2O_3$  beyond mere traces. Results for Wyoming bentonite in sodium carbonate solutions are shown in table 12 and figure 32.

The silica curve (fig. 32) is of the same general character as for acid (figs. 25 and 26). It rises to a low maximum at about 0.025 percent sodium carbonate, descends to a minimum at 0.05 percent, then rises steadily to a final maximum of 0.70 gram per liter at 1 percent sodium carbonate. At 0.005 percent the silica is a little higher than for pure water, instead of lower as with an acid. The first maximum is at one-tenth the concentration of the maximum for acid solutions. Up to 0.05 percent alkali there is no free carbonate in the filtered solution—the carbon dioxide is either released by the clay or retained upon it. At and above 0.1 percent sodium carbonate there is free carbonate in solution. At the second maximum (about 1.5 percent) as at the first (0.025 percent) there is apparently no net energy change in passing from clay to hydrosol. At intermediate concentrations, there appears to be a net energy difference. Although equilibrium is attained, the capacity for transfer is limited.

The ratio of dissolved silica to sodium carbonate is significant. If all the soda were used in producing  $Na_2Si_4O_9$  that ratio would be 2.30. However, the ratio found is a maximum (1.34) at low concentrations, is dropping rapidly at 0.02 percent, reaches a nearly constant value (0.26) through the critical range, then descends gradually to about 0.07 at one percent sodium carbonate.

#### ELECTRODIALYSIS OF HYDROSOLS

The experiments on the solubility of clay described above indicated the existence of a reversible equilibrium between clay, reagent (water plus acid or alkali), and product, as some clay and some reagent always remain free. The product is therefore not simply silica plus salt but some combination of silica with bases in equilibrium with clay and acid. Further evidence is the fact that silica is found in some solutions far in excess of the saturation limit.

In search for more direct information as to the nature of the product formed by clay and reagent solutions, some 35 of these solutions were electrodialyzed. A Mattson dializer with 1×10×15 centimeter cell, sheet platinum electrodes, and cellophane membranes was used. These membranes pass salts and silica hydrosols freely but not dialyzed iron. Current was limited to 0.8 ampere by a lamp in series. Electrode liquors were changed every hour for 3 or 4 hours then finished with an overnight run. Anode and cathode liquors were evaporated and analyzed separately. Silica, if any, remaining in the cell was determined.

TABLE 12.—Silica dissolved from Wyoming bentonite by solutions containing sodium carbonate

Percent $Na_2CO_3$ .....	0.0	0.005	0.01	0.02	0.05	0.1	0.2	0.5	1.0
$SiO_2$ in solution.....	0.064	0.067	0.132	0.178	0.133	0.260	0.397	0.598	0.700
$SiO_2:Na_2CO_3$ .....		1.34	1.32	.89	.266	.260	.200	.126	.070

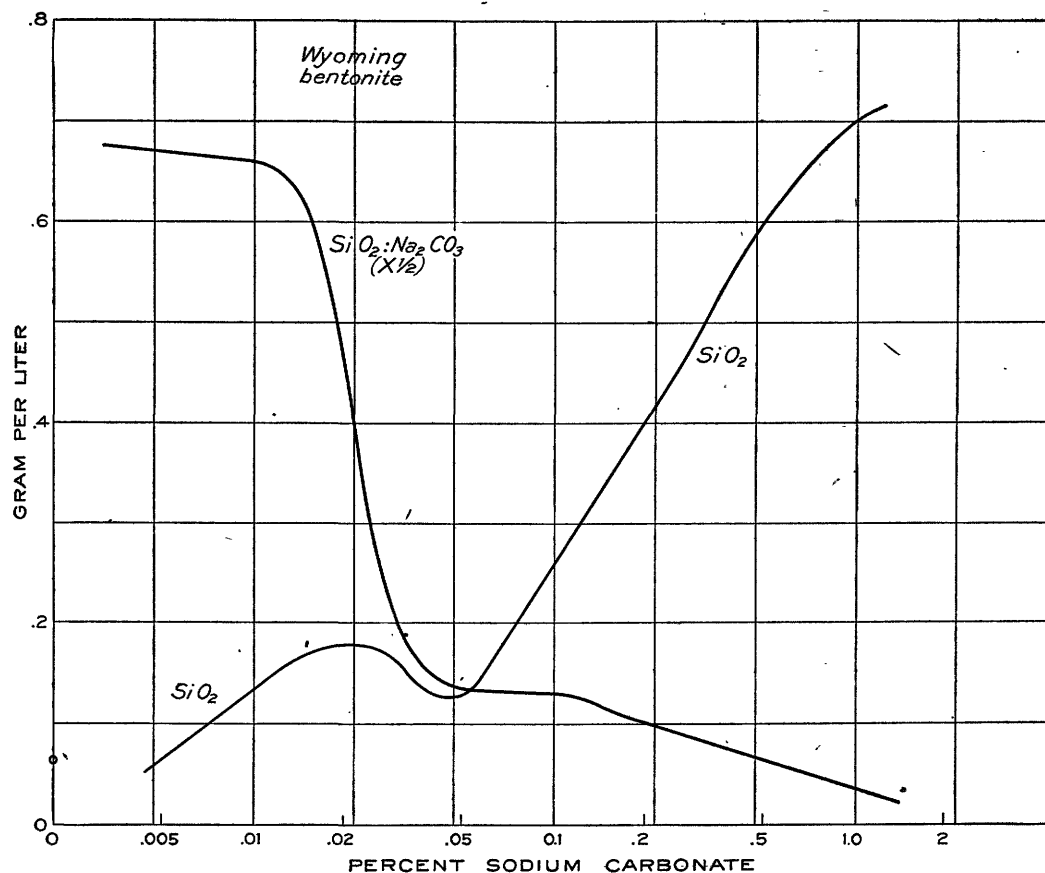


FIGURE 32.—Wyoming bentonite in sodium carbonate solutions.

A saturated solution of silica, evaporated to one-fourth volume was dialyzed. Of 0.1974 gram of total silica, 0.0610 was found with the positive ions, 0.0607 with the negative, 0.0180 still in the filtered cell solution, and 0.0577 as precipitated silica in the cell and on the membranes. As the transports of silica with and against the current are equal and the silica micella itself cannot be both positive and negative, it is evident that different micellae must carry equal and opposite charges as adsorbed H (or  $\text{H}_2\text{O}$ ) and OH ions. The precipitated silica remaining untransported indicates that possibly some micellae were stripped of their charges before they could be transported or else that there were insufficient H and OH ions present to supply them.

The same supersaturated silica solution with ammonium chloride or hydrochloric acid added to supply more free ions than water alone still gave equally divided silica but with more instead of less precipitated silica. A sodium silicate solution, diluted to about 30 grams per liter, also gave equal transport in the two directions with about half the total remaining in the cell. Equal transport was also found with most of the equilibrium clay solutions discussed below and many of these gave little or no cell residue. When sodium aluminate was

added to a saturated solution of pure silica and dialyzed, more than 96 percent of the silica was precipitated without transport. Despite the high affinity of both ions for silica, they rob it of its H and OH and leave it to coagulate.

When sodium chloride is added to a pure silica solution and dialyzed, twice as much silica goes with the positive ions as with the negative. A similar test with added aluminum chloride shows the opposite effect—5.5 percent positive, 13.1 percent negative, and 81.4 percent precipitated. A well-aged clear liquor from Wyoming bentonite (alkaline) plus water, showed twice as much positive (64.6 percent) as negative (33.5) silica, with almost none (1.9 percent) precipitated. The same liquor with hydrochloric acid added before dialysis gave nearly equal transport (48 against 44), while with sodium chloride added the transport was 95.5 positive against 4.5 negative.

Electrodialysis of equilibrium clay-acid solutions always gave silica nearly equally divided between positive and negative ions. The results of a few typical runs are given in table 13. The volume of filtrate stated was evaporated to 150 cubic centimeters for electrodialysis.

TABLE 13.—*Electrodialysis of clays*

Polkville clay in 0.2 percent hydrochloric acid, 1,575 milliliters filtrate					
	Total solids	Water insoluble	SiO <sub>2</sub>	Insoluble R <sub>2</sub> O <sub>3</sub>	CaO
Cations.....	1. 2886	0. 2754	0. 1170	0. 0927	0. 05580
Cell.....	. 3537	. 3340	. 2810	Trace	
Anions.....	. 5190	. 2155	. 1166	. 0272	. 1380
Quincy clay in 2 percent hydrochloric acid, 400 milliliters filtrate					
Cations.....	1. 4787	0. 1822	0. 0378	0. 0724	None
Cell.....	. 0300	. 0250	. 0100	. 0052	None
Anions.....	. 5956	. 3559	. 0368	. 1745	. 0402
Soil in 1 percent hydrochloric acid, 400 milliliters filtrate					
Cations.....	1. 0656	0. 1475	0. 0752	0. 0482	0. 0735
Anions.....	. 4547	. 2532	. 0834	. 1010	Trace
Acid-treated Filtrol in 1 percent hydrochloric acid, 400 milliliters filtrate					
Cations.....	1. 7601	0. 1605	0. 0535	0. 0455	0. 1219
Anions.....	. 5889	. 2827	. 0425	. 1115	. 0617
Quincy clay in 0.02 percent hydrochloric acid, 2,000 milliliters filtrate					
Cations.....	0. 6093	0. 1236	0. 0795	Trace	0. 3640
Cell.....	. 2077	. 1329	. 1885	None	None
Anions.....	. 1976	. 1040	. 0900	Trace	None
Quincy clay in 0.5 percent potassium hydroxide, 500 milliliters filtrate					
Cations.....	4. 9082	0. 2256	0. 2305	Trace	None
Cell.....	. 1128	. 0603	. 0375	None	None
Anions.....	1. 3084	. 4575	. 4185	None	None

Silica is transported nearly equally in both directions in every acid solution. With potassium hydroxide as solvent, nearly twice as much is transported as negative ions. No free ions are left in the cell, and in two cases, no silica even. Calcium is transported as anions in some cases. The R<sub>2</sub>O<sub>3</sub> is decidedly unbalanced, usually favoring the anions. That silica is balanced from the start was shown by separate analyses of the first cation and anion liquors removed.

Clay solutions are a complex mixture of salts and hydroxides of the amphoteric elements aluminum, iron, and silicon, together with magnesium and calcium, which function only as bases. Pure solutions and suspensions of the amphoteric hydroxides show equal transport as anions and cations when electrodialyzed. Aluminum hydroxide in water below about 50° C. is ionized as  $\text{AlOOH} \rightarrow \text{AlO}_2\text{H} + \text{AlO.OH}$ , and iron in like manner. Above about 50° C. each goes to a monohydrate, such as  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  diaspore. Hydrated silica  $\text{HSiO}_3\text{H}$  apparently ionizes as  $\text{HSiO}_3\text{H}$  and  $\text{HSiO}_2\text{OH}$ , as it shows equal transport with and against the current.  $\text{Ca(OH)}_2$  or  $\text{Mg(OH)}_2$  alone in water shows only cation

transport. In those experiments listed in table 13 where anion transport of calcium is shown, it was probably attached to one or several anions. To fully interpret the varied results shown in this table, much more experimental work on simpler systems will be required.

#### SUMMARY AND CONCLUSIONS

The solubility of a number of clays in acids and alkali of a wide range of concentrations indicates that the solution process is of at least three kinds for every clay, dependent on the concentration of solvent.

At equilibrium, a fraction of the acid or alkali remains free, and a fraction of each clay remains undissolved regardless of the proportions present. Hence, the reactions appear to be reversible, as indicated by varying equilibrium conditions.

Over a range of low acid concentrations, 0.05 to 0.2 normal, the "solution" is essentially a silicate hydrosol similar in composition to the clay dissolved. At higher concentrations it contains also salts in solution; at lower concentrations excess silica. At acid concentrations of 20 percent and over, bases but no silica go into solution and no hydrosols are formed.

Over a range of low alkali concentrations, 0.002 to 0.005 normal (0.02 to 0.05 percent) sodium carbonate, the solution is essentially an alkali silicate hydrosol, only silica being removed from the clay. At concentrations of alkali below the critical range, no carbonate is left in solution.

With montmorillonite clays the critical anion concentration is around 0.1 mole per liter while the critical cation ( $\text{Na}^+$ ) concentration is around 0.001 mole per liter. Within the critical acid range, the anions may be considered as competing on substantially equal terms with silicic acid for the bases of the clay. Within the critical alkali range, the alkali in solution is competing on equal terms with the bases of the clay for the silica.

A saturated solution (hydrosol) of pure silica is practically un-ionized and nearly nonconducting for electricity. When electrodialyzed, however, the silica is transported equally with cations and anions. Silica hydrosol, when stripped of adsorbed ions flocculates and precipitates in large aggregates. When concentrated, it goes over to a hydrogel at a concentration of about 5 percent.

A silicate hydrosol, stabilized with respect to clay and free acid, if electrodialyzed shows equal transport of silica in the two directions. It appears that a variety of ions are adsorbed in inverse proportion to their valence so that the total positive and negative charges are equal.

When alien ions are added to an equilibrium silicate hydrosol, electrodialysis no longer gives equal transport

of silica in the two directions if either cation or anion has an affinity for silica greater than that of H and OH, otherwise they have little effect on that balance.

In base-exchange work, it is well known that the nature of the anions as well as the bases must be taken into account. This investigation indicates that the concentrations of the anions present may also be of critical importance.

Defining "mineralizers" as added constituents which promote the deposition of crystalline solids from solution, it is evident that within the scope of this investigation no such agent exists. Even strong salt solutions diminish the concentration of silica solutions only to half saturation. Silica and silicate hydrosols go over to hydrogels on concentration, not to crystalline solids. Given sufficient time, however, they might form crystals.





## INDEX

	Page		Page
Calcium, determination of.....	230	Quincy clay, character of.....	227
Experimental procedure.....	219	electrodialysis of.....	232
Filtrol, electrodialysis of.....	232	solubility of, in acid solutions.....	222-224, 227, 228, 230
solubility of, in acid solutions.....	222-224, 227, 229	Silica, dialysis of.....	231
Hydrosols, electrodialysis of.....	230-233	solubility of, factors affecting.....	220, 222
Japanese clay, solubility of, in acid solutions.....	222-224, 226, 230	in hydrochloric acid solutions.....	220, 221
Mineralizer, definition of.....	222, 233	in water.....	220, 221
Montmorillonite clays, solubility of, in acid solutions.....	219, 222-230, 232	Soil, electrodialysis of.....	232
solubility of, in alkaline solutions.....	230, 232	solubility of, in acid solutions.....	222-224, 227, 228
Polkville clay, electrodialysis of.....	232	Wyoming bentonite, solubility of, in acid solutions.....	222-224, 227, 230
solubility of, in acid solutions.....	222-224, 227	solubility of, in alkaline solutions.....	231, 231
Purpose of the report.....	219		235



UNITED STATES DEPARTMENT OF THE INTERIOR  
Harold L. Ickes, Secretary  
GEOLOGICAL SURVEY  
W. C. Mendenhall, Director

---

Professional Paper 197

---

# SHORTER CONTRIBUTIONS TO GENERAL GEOLOGY

1941-42

---

PAPERS BY  
ESPER S. LARSEN, THOMAS B. NOLAN, P. G. NUTTING  
AND OTHERS



UNITED STATES  
GOVERNMENT PRINTING OFFICE  
WASHINGTON : 1943



# CONTENTS

[The letters in parentheses preceding the titles are those used to designate the individual papers]

	Page
(A) Alkalic rocks of Iron Hill, Gunnison County, Colorado, by Esper S. Larsen (published in March 1942).....	1
(B) Oligocene Foraminifera near Millry, Alabama, by Joseph A. Cushman and Winnie McGlamery (published in March 1942).....	65
(C) Lower Pennsylvanian species of <i>Mariopteris</i> , <i>Eremopteris</i> , <i>Diplothmema</i> , and <i>Aneimites</i> from the Appalachian region, by David White (published in —1943).....	85
(D) The Basin and Range province in Utah, Nevada, and California, by Thomas B. Nolan (published in —1943).....	141
(E) Some standard thermal dehydration curves of minerals, by P. G. Nutting (published in —1943).....	197
(F) The action of some aqueous solutions on clays of the montmorillonite group, by P. G. Nutting (published in —1943).....	216

# ILLUSTRATIONS

	Page
PLATE 1. Geologic map of Iron Hill area, Gunnison County, Colo.....	In pocket
2. Panorama of the Iron Hill area.....	2
3. A, B, Pyroxenite on south side of Stone Gulch; C, Banded syenite.....	18
4. Miliolidae, Ophthalmitidae, Lagenidae, and Polymorphinidae.....	78
5. Polymorphinidae, Nonionidae, Heterohelicidae, and Buliminidae.....	79
6. Buliminidae, Ellipsoidinidae, and Rotaliidae.....	80
7. Rotaliidae, Amphisteginidae, Cassidulinidae, Anomalinidae, and Planorbulinidae.....	81
8-39. Species of <i>Mariopteris</i> , <i>Eremopteris</i> , <i>Diplothmema</i> , and <i>Aneimites</i> .....	105
40. Stratigraphic sections of Paleozoic sedimentary rocks in belts parallel to the axis of the Cordilleran geosyncline.....	152
41. Stratigraphic sections of Paleozoic sedimentary rocks in belts normal to the axis of the Cordilleran geosyncline.....	152
FIGURE 1. Marble-pyroxenite contact.....	5
2. Section south of Stone Gulch, showing variation in pyroxenite.....	17
3. Section on north side of Stone Gulch, showing variation in pyroxenite.....	18
4. Section south of Deldorado Creek, showing variation in pyroxenite.....	18
5. Section northeast of gully B, showing complex relations of uncomphagrite and varieties of pyroxenite.....	19
6. Pseudo-binary diagram of equilibrium in mixtures of nepheline and diopside.....	24
7. Optical properties of the pyroxenes carrying acmite plotted against content of $Fe_2O_3$ and acmite.....	48
8. Soda tremolite and glaucophane amphiboles, atomic ratios plotted against $Mg + Fe'' - Al - Fe'''$ .....	51
9. Soda tremolite and glaucophane amphiboles, $\beta$ , $Y/\alpha$ , and specific gravity plotted against $Mg + Fe'' - Al - Fe'''$ .....	51
10. Map showing outlines of the portion of the Basin and Range province described in this paper and the localities to which reference is made.....	143
11. Map of the Pleistocene lakes in the Great Basin region.....	170
12. Distribution of known thrust faults in the Great Basin region.....	175
13. Block faulting in three areas in Utah: A, Stockton and Fairfield quadrangles; B, A portion of the southern Wasatch Range; C, Gold Hill quadrangle.....	181
14. Curves of slight curvature variation.....	200
15. Curves for hydrous oxides and zeolites.....	202
16. Curves for hydrous oxides and related silicates.....	204
17. Curves for the kaolin group.....	206
18. Curves for montmorillonites.....	208
19. Curves for the montmorillonite group.....	210
20. Curves for chlorites and related silicates.....	212
21. Curves for micas.....	214
22. Curves for carbonates.....	216
23. Solubility of opaline silica in water at different temperatures.....	221
24. Solubility of silica in hydrochloric acid solutions.....	221
25. Wyoming bentonite in hydrochloric acid solutions.....	225
26. Wyoming bentonite in oxalic acid solutions.....	225
27. Japanese acid clay in hydrochloric acid solutions.....	226
28. Polkville bentonite in hydrochloric acid solutions.....	226
29. Quincy clay (Florida fuller's earth) in hydrochloric acid solutions.....	228
30. Soil in hydrochloric acid solutions.....	228
31. Filtrol (activated bentonite) in hydrochloric acid solutions.....	229
32. Wyoming bentonite in sodium carbonate solutions.....	231